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(54) THERMALLY EXPANDABLE MICROCAPSULE AND ITS PRODUCTION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a process for producing a thermally expandable microcapsule which is a microcapsule expanded by heating at a prescribed temp., exhibits stable foamability and has excellent preservation stability.

SOLUTION: The shell of the microcapsule consists of a polymer obtd. by adding a radial polymn. ratio monomer (II) contg. a carboxyl group, and if necessary, a monomer (III) having ≥ 2 polymn. ratio double bonds, a monomer (IV) which is a component for regulating the softening point and a hydrophobic monomer (V) to an acrylate and/or methacrylate monomer (I) having a range of $T_g=50$ to 20 as the monomer which is the essential component of the shell and polymerizing the added monomer mixture. The microcapsule has the shell and contains ≥ 1 liquid having the b.p. below the softening point of the polymers. The water phase comprises a dispersion system consisting of a polysiloxane inorg. polymer gel, a water-soluble high-molecular dispersant and $\geq 10\%$ concn. aq. inorg. salt soln. polymerizable monomer mixture. The non-aq. liquid to be sealed into the microcapsule and a radical reaction initiator is dispersed and is then subjected to in-situ polymn.

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CLAIMS

[Claim(s)]

[Claim 1] It is the acrylate and/or the methacrylate system monomer (I) used as the range whose monomer used as a principal component is $T_g=50-200$ degree C. The radical polymerization nature monomer (II) containing a carboxyl group, and the monomer which has two or more polymerization nature double bonds as occasion demands (III), The microcapsule which connotes one or more liquids which make an outer shell the polymer obtained by adding the monomer (IV) and hydrophobic monomer (V) which are the component which adjusts softening temperature, and carrying out a polymerization, and have the boiling point below the softening temperature of this polymer.

[Claim 2] The thermal-expansion microcapsule according to claim 1 characterized by the endocyst gas retention after 50-degree-C one-month preservation being 60% or more.

[Claim 3] The thermal-expansion nature microcapsule according to claim 1 characterized by carrying out cubical expansion to 7 or more times with heating for 130 degree-Cx 1 minute.

[Claim 4] in after an aqueous phase-less distribute the mixture of the nonaqueous nature liquid enclose by the polymerization nature monomer mixture which have a partial saturation double bond, and the interior into the distributed drainage system which consist of dispersed systems which consist of a mineral salt water solution more than polysiloxane inorganic polymer gel, a water-soluble molecular dispersion agent, and 10% concentration, and come to adjust a drainage system pH to 2-7, and a radical reaction initiator the microcapsule manufacture approach characterize by carry out a situ polymerization.

[Claim 5] The manufacture approach according to claim 4 which a polymerization initiator is oil solubility peroxide or azobis system compound, and is characterized by using what has the half-life of 1 - 10 hours with reaction temperature.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the thermal-expansion nature microcapsule which passed with fizz and was excellent in the Tokiyasu quality, its manufacture approach, and its use.

[0002]

[Description of the Prior Art] More examination than before has been made by the thermal-expansion nature microcapsule which confined the low boiler in the endocyst object by using a thermoplastic polymer as a wallplate. For example, they are JP,42-286534,B, JP,55-17372,A, etc. The former is related with the general manufacture approach about a thermal-expansion nature microcapsule. The 2nd patent is the approach of removing the survival of an acrylonitrile monomer from a thermal-expansion microcapsule after a reaction, and the acrylonitrile system monomer is used as a principal component of a microcapsule. Moreover, the 3rd approach is using acrylonitrile for a principal component too, and cannot remove it from the configuration of a microcapsule. Use of acrylonitrile is required of these thermal-expansion nature microcapsules. Since the thickness of wall membrane decreases also from 1/10 of origin to 1/100 at the time of heating expansion, by the usual polymer, the gas by which endocyst is carried out through wall membrane will penetrate a thermal-expansion nature capsule, and it will be contracted rapidly. In order not to contract but to make a configuration hold also in the time of heating, the polymer of gas barrier nature had to be used, but unless it surely used one kind among acrylonitrile, the methacrylonitrile, the vinylidene chloride, and the vinylchloride monomer for the reason, the good foaming microcapsule was not obtained.

[0003] The volume increases by carrying out heating expansion including a low boiler into a single nucleus, and a thermal-expansion nature microcapsule forms a closed cell into the resin, when mixed in resin. Therefore, since a concavo-convex pattern is displayed on a resin front face, it is used for wallpaper, a solid print, a solid copy system, etc. In recent years, an environmental problem is being regarded as questionable on a scale of terrestrial. We are anxious about the damage over are recording by not disassembling synthetic macromolecule. Moreover, in Japan with much incineration processing, it is greatly regarded as questionable also in the toxic gas which occurs at the time of combustion. It leads also to a toxic gas occurring and it causing secondary disaster in case of a fire, and a pollution-free foaming agent has been desired especially in the U.S. with much use, such as wallpaper, and Europe. In relation to this, the foaming ratio microcapsule made EKOTAIPU the microcapsule which does not use the monomer of the Krol system, i.e., a vinylidene chloride, and a vinyl chloride, and although Kamiichi had been carried out, it was inadequate when saying from the effect on an environmental safety aspect and the body still more.

[0004]

[Problem(s) to be Solved by the Invention] Conventionally, in the thermal-expansion nature microcapsule, development has advanced by making into wall membrane the acrylic polymer copolymer which used acrylonitrile and a vinylidene chloride as the principal component. They are in. It is the approach from which a microcapsule is obtained simple by application of a

suspension-polymerization method by the situ polymerization, and acrylonitrile and a vinylidene chloride also had the ease of access referred to as being used for fiber and a food-grade packing material. we should examine the problem over current environmental pollution seriously, and a microcapsule should be created for a material with high safety — ** — as a result of inquiring wholeheartedly in a technical problem (acrylonitrile, meta-chestnut RORONI tolyl, a vinylidene chloride, and a vinyl chloride are not included), it came to complete this invention.

[0005]

[Means for Solving the Problem] A polymer with a small gas transmission coefficient is required of the homopolymer obtained from monomers other than acrylonitrile, a methacrylonitrile, and a vinylidene chloride. Then, we examined the monomer which fulfills the following conditions.

(1) A molecule is comparatively small and tends to take the crystal structure.

(2) Film formation nature serves as a good high coat.

There are very few monomers which fulfill this condition, and the monomer which is moreover easy to take the crystal structure has very high water solubility. Therefore, at the usual reaction, since it is hard to be obtained, a microcapsule needs a device a little to use this monomer as a principal component.

[0006] We examined the conditions for using the monomer of this network paying attention to the polymer of a polyvinyl alcohol system and a polycarboxylic acid system having crystal structure construction nature, and having big drag force to gas vitrification nature. However, water solubility is very high although the gas transmission coefficient of a polyvinyl alcohol system polymer is small. Moreover, in order to have to saponify installation of a hydroxymethyl group after copolymerization of vinyl acetate, a thermal-expansion ratio microcapsule is not obtained. It has [polycarboxylic acid / at an acid type] water solubility to it and is stable. When maintaining the product at an acid - the acescence, it turned out that a function is fully achieved as a microcapsule coat. Moreover, since affinity is high, it is also rare to make an endocyst solvent penetrate, and the holdout of gas is also good.

[0007] On condition that reaction time, the monomer of an acrylic-acid system has high water solubility, and a good capsule is not obtained by the creation approach of the usual microcapsule. In the usual dispersed system, a monomer is distributed underwater, and it is in from an oil phase. Although a situ polymerization generates a polymer wall, it is because there is no force in which the creation approach of this capsule limits the acrylic-acid mold monomer to the oil phase. Then, the soluble high matter, i.e., mineral, is added in the aqueous phase to dissolve an acrylic acid into an oil phase, and the forcible distribution of the acrylic acid are carried out into an oil phase according to a salting out effect. Canal ratio monomers, such as styrene, are added if needed, and distributivity is raised further. Since the hydrophilic property is high, an acrylic acid should exist in a near place according to an interface, and the shell outer layer should serve as acrylic-acid Rich's presentation. Then, the meeting nature of carboxylic acids comes out, and crystallinity fully goes up and comes to discover sufficient function as a fizz microcapsule.

[0008] It came to invent the thermal-expansion nature microcapsule in which intermolecular distance becomes from a short polymer, stable endocyst gas holdout is shown, and stable fizz is shown in a predetermined temperature field from that of a more than. Namely, the thermal-expansion nature microcapsule of this invention is the acrylate and/or the methacrylate system monomer (I) used as the range whose monomer used as a principal component is $T_g=50-200$ degree C. The radical polymerization nature monomer (II) containing a carboxyl group, and the monomer which has two or more polymerization nature double bonds as occasion demands (III), The polymer obtained by adding the monomer (IV) which is the component which adjusts softening temperature, and carrying out a polymerization is made into an outer shell, and it is characterized by connoting one or more liquids which have the boiling point below the softening temperature of this polymer. moreover, the manufacture approach of this invention be in after an aqueous phase distribute the mixture of the nonaqueous nature liquid enclose by the polymerization nature monomer mixture which have a partial saturation double bond, and the interior into the distributed drainage system which consist of dispersed systems which consist of polysiloxane inorganic polymer gel, a water soluble polymer dispersant, and a mineral salt water solution more than 10-% concentration, and come to adjust a drainage system pH to 2-7, and a

radical reaction initiator. it be characterize by carry out a situ polymerization.

[0009] The polymerization nature monomer used for this invention is classified into some groups. The following are used as a compound of the radical reaction nature which has a partial saturation double bond.

It is the component which forms the Ith component frame, and the monomer which Tg is comparatively high and moreover has film formation nature is used. What what serves as the range of 50-200 degrees C by the homopolymer as Tg was used, and was indicated below is desirable. The amount used is preferably [40 - 80% of] good 20 to 99%. Methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, t-butyl methacrylate, isobornyl (meta) acrylate, cyclohexyl methacrylate, benzyl methacrylate, etc.

[0010] the — although a carboxylic-acid radical is contained in monads, such as II component acrylic acid, a methacrylic acid, a succinic acid, and an itaconic acid, it is not limited to what was indicated. The content is 10 - 30% preferably one to 40% of the weight. At less than 1 % of the weight, if gas barrier nature is not enough and, on the other hand, exceeds 40 % of the weight, a microcapsule will not be obtained.

[0011] the — the optimal amount changes with a class, an amount, and reactant differences of the cross linking agent component which gives rubber elasticity to an III component outer wall coat. It is easy to be the monomer which has a radical polymerization nature double bond two or more fundamentally. The amount used is preferably [0.1 - 1.0% of] good 0 to 5%. Although an example is described below, it is not limited to this. Ethylene GURIKORUJI (meta) acrylate, propylene GURIKORUJI (meta) acrylate, Diethylene GURIKORUJI (meta) acrylate, 1, 4-butane JIORUJI (meta) acrylate, 1, 6-hexane JIORUJI (meta) acrylate, TORIMECHI roll pro pantry (meta) acrylate, GURISERINJI (meta) acrylate, TORIECHIRENGURIKORUJI (meta) acrylate, PEG#200 di(meth)acrylate, PEG#400 di(meth)acrylate, PEG#600 di(meth)acrylate, 1, 3-butane JIORUJI (meta) acrylate, Neopentyl GURIKORUJI (meta) acrylate, 1, 10-decane JIORUJI (meta) acrylate, Pen TAERISURITORUTORI (meta) acrylate, pentaerythritol tetrapod (meta) acrylate, Pentaerythritol hexa (meta) acrylate 3-AKURO yloxy glycerol monoacrylate, dimethylol tricyclo DEKANJI (meta) acrylate, triaryl HORUMARUTORI (meta) acrylate, a divinylbenzene, etc.

[0012] the — by the monomer which carries out the auxiliary role of the Ith component of IV component, the improvement of a rate of reaction, softening temperature, and gas barrier nature is borne. That whose Tg of a homopolymer is -20-40 degree C is good. The amount used is 2 - 10% preferably 1 to 20%. Although there are methyl acrylate, ethyl acrylate, vinyl acetate, a methyl ethyl ketone, etc., it is not limited to what was indicated.

[0013] the [Vth component] — as a hydrophobic monomer which suppresses the water solubility by the increment in II component, it adds as occasion demands and the amount used is 5 - 20% preferably 0 to 30%. Styrene, 1,3-butadiene, an isobutylene, 1-pentene, 2-pentene, a 2-methyl-1-butene, a 2-methyl-2-butene, a propylene, 1-octene, etc.

[0014] Generally in actual creation, the fizz microcapsule creation approach from the former is used. That is, a dispersant uses the gel of a colloidal silica system as a drainage system. A water soluble polymer compound is used as an auxiliary dispersant. As for a water soluble polymer compound, a diethanolamine-adipic-acid condensate, a polyvinyl pyrrolidone, methyl cellulose, etc. are used. Moreover, in order to use a lot of water-soluble monomers for this invention, an inorganic metal salt is used. The compound which dissolves in water as a water-soluble metal salt in neutrality, such as a sodium chloride, a magnesium chloride, sodium sulfate, a calcium chloride, and magnesium sulfate, or an acid field is used. More than 10% concentration of the water to be used is required for the amount used. If an inorganic metal salt is not used, even if it is hard to form a microcapsule and forms, by this monomer presentation, gas barrier nature will be inferior (the endocyst gas retention after 50 degree-C one-month preservation is 40% or less). the above-mentioned mixture — pH 2-7 — it prepares to pH 2-5 preferably, and considers as a distributed drainage system.

[0015] An oil phase is mixed and used for homogeneity. Monomer mixture with partial saturation duplex association of radical reaction nature, the solvent mixture which has the boiling point below the softening temperature of an outside cereals polymer, and a radical initiator are used as an oil phase. By not dissolving in an outer wall polymer, although the organic solvent with which a

solvent has the boiling point below **** temperature is used, although anything can be used if foaming effectiveness is high, the solvent of the hydrocarbon mold of the -20 - 100 boiling point range fits use. A petroleum fractional distillation component, such as n-butane, an isobutane, n pentane, an isopentane, a neopentane, n-hexane, an isohexane, n-heptane, and the other petroleum ether, is used timely.

[0016] The catalyst whose half-life temperature is 20 degrees or more is used for a radical initiator for 10 hours. as the catalyst which can be used — a peroxide mold and an azobis mold — although any are sufficient, in order to carry out little content of the nitrile group in the initiator of an azobis mold at intramolecular — desirable — peroxidation — a snout — type or the azobis mold which does not contain a nitrile group is used. The thing of the 45-100 degree-C range has a preferably good 10-hour half-life 30 to 130 degree C. Although what does not specifically contain a nitrile group among diisopropyl peroxy carbonate, dioctyl peroxy dicarbonate, t-butyl-peroxy-laurate, lauroyl peroxide, dioctanoyl peroxide, benzoyl peroxide, azobisisobutyronitril, azobis (2,4-dimethylvaleronitrile), 1, and 1-azobis (cyclohexane-1-carbonitrile), dimethyl 2, 2'-azobis (2-methyl propionate), etc. is desirable, it is not limited to what was indicated.

[0017]

[Example] It is NaCl in 600g of example 1 ion exchange water. 200g is dissolved. 1g of adipic-acid diethanolamine condensates which are a ***** polymer is dissolved, and 100g of colloidal-silica 20% water solutions is added. This water solution is prepared to pH3.5, and it considers as the aqueous phase. Methacrylic acid methyl (MMA) 170g, methyl-acrylate (MA)10g, acrylic-acid (AA)20g, EDMA 1g, azobisisobutyronitoriru 1g is mixed and it considers as a homogeneity solution. Let an isobutane in an autoclave be 50g preparation homogeneity solution at a monomer phase. After adding the aqueous phase here and adjusting particle diameter to ten to 25 micrometer, a nitrogen purge is carried out and it is made to react with the reaction temperature of 70 degrees C for 8 hours. Reaction pressure was performed by 0.8MPa(s) and stirring was performed by 500rpm. It was opened to traffic, although it cooled after reaction termination and let the screen of 150 meshes pass. It was air-dry after filtration. The particle size of the obtained microcapsule was 23 micrometers (a laser diffraction type particle-size-distribution measuring instrument (JEOL HELOS & RODOS (product made from German SYMPATEC GmbH)) is used for particle size, and it says the particle size used as 50% of accumulation of volume particle size distribution).

[0018] It coated on the test paper so that the obtained microcapsule might be mixed with an ethylene vinyl acetate system emulsion by the solid content ratio 2:1 and it might become 100-micrometer thickness at the time of desiccation. The heating foaming trial was performed in oven and it expanded to thickness 10 times in 130 degree-Cx 1 minute. The fizz of a microcapsule has 7 or more desirable times at 130 degree-Cx 1 minute, and is more desirable at 150 more degree-Cx 1 minute. [of 4 or more times] Moreover, although endocyst capacity was measured after one-month preservation at 50 degrees C in order to see the shelf life of the gas in a microcapsule, 80% of the initial intensive matter remained. In this invention, 60% or more, it is more desirable and manufacture of 80% or more of thing of the gas shelf life of a microcapsule is attained.

[0019] Example 2 aqueous phase is adjusted like an example 1. Methacrylic acid methyl (MMA) 55g, methacrylic acid ethyl (EMA) 55g, methyl-acrylate (MA)10g, acrylic-acid (AA)50g, (Styrene St) 30g, EDMA 1g and azobis (2,4-dimethylvaleronitrile) 1g are mixed, and it considers as a homogeneity solution. In an autoclave, 25g is taught to a monomer phase and let isobutane 25g and an isopentane be oil phases at it. After adding the aqueous phase here and preparing particle diameter to ten to 25 micrometer, a nitrogen purge is carried out and it is made to react with the reaction temperature of 60 degrees C for 8 hours. Reaction pressure was performed by 0.8MPa (s) and stirring was performed by 500rpm. The expansion scale factor was measured with the same test method as an example 1, and it expanded to thickness 12 times in 130 degree-Cx 1 minute. Moreover, although endocyst capacity was measured after one-month preservation at 50 degrees C in order to see the shelf life of the gas in a microcapsule, 95% of the initial intensive matter remained.

[0020] It manufactured like **** and the example 1 which show an example 3-12 in Table 1.
[Table 1]

テストNo.	実施例1	実施例2	実施例3	実施例4	実施例5	実施例6	実施例7	実施例8	実施例9	実施例10	実施例11	実施例12
MMA	170	55	170	170	170	110	40		160	170	170	170
EMA		55						170				
VAc									20			
MA	10	10	10	10	10	10	20	10	20	10	10	10
AA	20		20	20	20	50	80	20	20		20	20
MAA										20		
St		30				20	60					
DVB											1	
EDMA	1	1	1	1	1	1	1	1	1	1		2
AIBN	1	1	1	1	1	1	1	1	1	1	1	1
イソブタン	50	25	20		30	50	50	50	50	50	50	50
イソペンタン		25	20									
イソヘキサン				50								
H ₂ O	600	600	600	600	600	600	600	600	600	600	600	600
NaCl	200	200	150	150			200	200	200	200	200	200
CaCl ₂						200						
MgCl ₂					200							
水溶性ポリアミド	2	2			2	2	2	2	2	2	2	2
メチルセルロース			2									
PVP				2								
反応温度 (°C)	70	60	70	70	70	70	70	70	70	70	70	70
反応時間 (hr)	8	8	8	8	8	8	8	8	8	8	8	8
収率 (400 (D x 50%)	23	22	25	21	24	25	22	19	26	21	24	23
加熱温度 (°C)	130	130	140	150	130	130	130	120	130	140	130	130
加熱時間	1	1	1	1	1	1	1	1	1	1	1	1
発泡倍率	10.5	12.5	8.1	4.5	5	11.7	5.8	7.8	7.1	3.2	9.1	7.2
内包ガス量	17.5	20.0	18.1	19	11	17	18.4	17.8	18.2	18.5	18	17.7
内包ガス量 (v/v) 50°C x 1ヶ月	14	18.9	16.2	18.5	8	16.0	16.1	14.1	15.0	14.3	18.9	14.1

[0021] The example of a comparison is given to Table 2.

When the examples 1 and 4 of a comparison and 5 acrylic acids are not used. Although foamed to the microcapsule which created the methyl methacrylate and the methyl acrylate as a principal component without the acrylic acid in the example 1 a little, there is no shelf life further low [expansion ratio], and outgassing happens immediately. Even if it changes a principal component similarly, when there is no acrylic acid, there are not fizz and a preservation ratio. It reacted by the example and the similar presentation except having made the amount of the example of comparison 2 acrylic acid used into 2.5%. In this case, the holdout of gas is bad although fizz is improved.

When the amount of the example of comparison 3 acrylic acid used was made into 50%, a microcapsule did not generate.

[0022]

[Table 2]

テストNo.	比較例1	比較例2	比較例3	比較例4	比較例5
MMA	180	185	90	150	150
St				30	
MA	20	10	10	20	
VAc					50
AA		5	100		
EDMA	1	1	1	1	1
AIBN	1	1	1	1	1
イソブタン	50	50	50	50	50
H ₂ O	600	600	600	600	600
NaCl	150	100	200	150	150
水溶性ポリアミド	2	2	2	2	2
コロイドシリカ	100	100	100	100	100
pH	3.5	3.5	3.5	3.5	3.5
反応温度 (°C)	70	70	70	70	70
反応時間 (hr)	8	8	8	8	8
粒径 (μm) (D _{x50%})	23	21		27	25
加熱温度 (°C)	130	130		130	130
加熱時間 (分)	1	1		1	1
発泡倍率	3.1	3.5		2.7	2.1
内包量 (wt%)	17	18		17.5	17.3
内包量 (wt%) 50°C×1ヶ月	3.4	5.2		2.1	2.5

[0023]

[Effect of the Invention] Although current [PVC] is mainly used, since ***** (chlorine, cyanogen, etc.) generate wallpaper at the time of combustion and incineration, examination of the ecology wallpaper of the resin use which does not contain halogens, such as EVA and an acrylic, and a nitro group is advanced. However, although an organic blowing agent, the thermal-expansion nature microcapsule containing conventional acrylonitrile, etc. are considered as a foaming agent of wallpaper, since all contain the nitro group, perfect ecology wallpaper (a halogen and a nitro group are not included) cannot be created. Moreover, although the ceramic of porosity, an electrode, a casting, etc. think as a hollow filler using the microcapsule after expansion etc., we are anxious about generating of a toxic gas (a halogen, nitro group) in the case of baking. Then, the problem of toxic gas generating is solved by using the thermal-expansion ratio capsule of this invention which does not contain a halogen and a nitro group.

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TECHNICAL FIELD

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[0003] The volume increases by carrying out heating expansion including a low boiler into a single nucleus, and a thermal-expansion nature microcapsule forms a closed cell into the resin, when mixed in resin. Therefore, since a concavo-convex pattern is displayed on a resin front face, it is used for wallpaper, a solid print, a solid copy system, etc. In recent years, an environmental problem is being regarded as questionable on a scale of terrestrial. We are anxious about the damage over are recording by not disassembling synthetic macromolecule. Moreover, in Japan with much incineration processing, it is greatly regarded as questionable also in the toxic gas which occurs at the time of combustion. It leads also to a toxic gas occurring and it causing secondary disaster in case of a fire, and a pollution-free foaming agent has been desired especially in the U.S. with much use, such as wallpaper, and Europe. In relation to this, the foaming ratio microcapsule made EKOTAIPU the microcapsule which does not use the monomer of the Krol system, i.e., a vinylidene chloride, and a vinyl chloride, and although Kamiichi had been carried out, it was inadequate when saying from the effect on an environmental safety aspect and the body still more.

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[Effect of the Invention] Although current [PVC] is mainly used, since ***** (chlorine, cyanogen, etc.) generate wallpaper at the time of combustion and incineration, examination of the ecology wallpaper of the resin use which does not contain halogens, such as EVA and an acrylic, and a nitro group is advanced. However, although an organic blowing agent, the thermal-expansion nature microcapsule containing conventional acrylonitrile, etc. are considered as a foaming agent of wallpaper, since all contain the nitro group, perfect ecology wallpaper (a halogen and a nitro group are not included) cannot be created. Moreover, although the ceramic of porosity, an electrode, a casting, etc. think as a hollow filler using the microcapsule after expansion etc., we are anxious about generating of a toxic gas (a halogen, nitro group) in the case of baking. Then, the problem of toxic gas generating is solved by using the thermal-expansion ratio capsule of this invention which does not contain a halogen and a nitro group.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] Conventionally, in the thermal-expansion nature microcapsule, development has advanced by making into wall membrane the acrylic polymer copolymer which used acrylonitrile and a vinylidene chloride as the principal component. They are in. It is the approach from which a microcapsule is obtained simple by application of a suspension-polymerization method by the situ polymerization, and acrylonitrile and a vinylidene chloride also had the ease of access referred to as being used for fiber and a food-grade packing material. we should examine the problem over current environmental pollution seriously, and a microcapsule should be created for a material with high safety — ** — as a result of inquiring wholeheartedly in a technical problem (acrylonitrile, meta-chestnut RORONI tolyl, a vinylidene chloride, and a vinyl chloride are not included), it came to complete this invention.

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MEANS

[Means for Solving the Problem] A polymer with a small gas transmission coefficient is required of the homopolymer obtained from monomers other than acrylonitrile, a methacrylonitrile, and a vinylidene chloride. Then, we examined the monomer which fulfills the following conditions.

(1) A molecule is comparatively small and tends to take the crystal structure.

(2) Film formation nature serves as a good high coat.

There are very few monomers which fulfill this condition, and the monomer which is moreover easy to take the crystal structure has very high water solubility. Therefore, at the usual reaction, since it is hard to be obtained, a microcapsule needs a device a little to use this monomer as a principal component.

[0006] We examined the conditions for using the monomer of this network paying attention to the polymer of a polyvinyl alcohol system and a polycarboxylic acid system having crystal structure construction nature, and having big drag force to gas vitrification nature. However, water solubility is very high although the gas transmission coefficient of a polyvinyl alcohol system polymer is small. Moreover, in order to have to saponify installation of a hydroxymethyl group after copolymerization of vinyl acetate, a thermal-expansion ratio microcapsule is not obtained. It has [polycarboxylic acid / at an acid type] water solubility to it and is stable. When maintaining the product at an acid - the acescence, it turned out that a function is fully achieved as a microcapsule coat. Moreover, since affinity is high, it is also rare to make an endocyst solvent penetrate, and the holdout of gas is also good.

[0007] On condition that reaction time, the monomer of an acrylic-acid system has high water solubility, and a good capsule is not obtained by the creation approach of the usual microcapsule. In the usual dispersed system, a monomer is distributed underwater, and it is in from an oil phase. Although a situ polymerization generates a polymer wall, it is because there is no force in which the creation approach of this capsule limits the acrylic-acid mold monomer to the oil phase. Then, the soluble high matter, i.e., mineral, is added in the aqueous phase to dissolve an acrylic acid into an oil phase, and the forcible distribution of the acrylic acid are carried out into an oil phase according to a salting out effect. Canal ratio monomers, such as styrene, are added if needed, and distributivity is raised further. Since the hydrophilic property is high, an acrylic acid should exist in a near place according to an interface, and the shell outer layer should serve as acrylic-acid Rich's presentation. Then, the meeting nature of carboxylic acids comes out, and crystallinity fully goes up and comes to discover sufficient function as a fizz microcapsule.

[0008] It came to invent the thermal-expansion nature microcapsule in which intermolecular distance becomes from a short polymer, stable endocyst gas holdout is shown, and stable fizz is shown in a predetermined temperature field from that of a more than. Namely, the thermal-expansion nature microcapsule of this invention is the acrylate and/or the methacrylate system monomer (I) used as the range whose monomer used as a principal component is $T_g=50-200$ degree C. The radical polymerization nature monomer (II) containing a carboxyl group, and the monomer which has two or more polymerization nature double bonds as occasion demands (III), The polymer obtained by adding the monomer (IV) which is the component which adjusts softening temperature, and carrying out a polymerization is made into an outer shell, and it is characterized by connoting one or more liquids which have the boiling point below the softening

temperature of this polymer. moreover, the manufacture approach of this invention be in after an aqueous phase distribute the mixture of the nonaqueous nature liquid enclose by the polymerization nature monomer mixture which have a partial saturation double bond, and the interior into the distributed drainage system which consist of dispersed systems which consist of polysiloxane inorganic polymer gel, a water soluble polymer dispersant, and a mineral salt water solution more than 10-% concentration, and come to adjust a drainage system pH to 2-7, and a radical reaction initiator. it be characterize by carry out a situ polymerization.

[0009] The polymerization nature monomer used for this invention is classified into some groups. The following are used as a compound of the radical reaction nature which has a partial saturation double bond.

It is the component which forms the Ith component frame, and the monomer which Tg is comparatively high and moreover has film formation nature is used. What what serves as the range of 50-200 degrees C by the homopolymer as Tg was used, and was indicated below is desirable. The amount used is preferably [40 - 80% of] good 20 to 99%. Methyl methacrylate, ethyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, t-butyl methacrylate, isobornyl (meta) acrylate, cyclohexyl methacrylate, benzyl methacrylate, etc.

[0010] the — although a carboxylic-acid radical is contained in monads, such as II component acrylic acid, a methacrylic acid, a succinic acid, and an itaconic acid, it is not limited to what was indicated. The content is 10 - 30% preferably one to 40% of the weight. At less than 1 % of the weight, if gas barrier nature is not enough and, on the other hand, exceeds 40 % of the weight, a microcapsule will not be obtained.

[0011] the — the optimal amount changes with a class, an amount, and reactant differences of the cross linking agent component which gives rubber elasticity to an III component outer wall coat. It is easy to be the monomer which has a radical polymerization nature double bond two or more fundamentally. The amount used is preferably [0.1 - 1.0% of] good 0 to 5%. Although an example is described below, it is not limited to this. Ethylene GURIKORUJI (meta) acrylate, propylene GURIKORUJI (meta) acrylate, Diethylene GURIKORUJI (meta) acrylate, 1, 4-butane JIORUJI (meta) acrylate, 1, 6-hexane JIORUJI (meta) acrylate, TORIMECHI roll pro pantry (meta) acrylate, GURISERINJI (meta) acrylate, TORIECHIRENGURIKORUJI (meta) acrylate, PEG#200 di(meth)acrylate, PEG#400 di(meth)acrylate, PEG#600 di(meth)acrylate, 1, 3-butane JIORUJI (meta) acrylate, Neopentyl GURIKORUJI (meta) acrylate, 1, 10-decane JIORUJI (meta) acrylate, Pen TAERISURITORUTORI (meta) acrylate, pentaerythritol tetrapod (meta) acrylate, Pentaerythritol hexa (meta) acrylate 3-AKURO yloxy glycerol monoacrylate, dimethylol tricyclo DEKANJI (meta) acrylate, triaryl HORUMARUTORI (meta) acrylate, a divinylbenzene, etc.

[0012] the — by the monomer which carries out the auxiliary role of the Ith component of IV component, the improvement of a rate of reaction, softening temperature, and gas barrier nature is borne. That whose Tg of a homopolymer is -20-40 degree C is good. The amount used is 2 - 10% preferably 1 to 20%. Although there are methyl acrylate, ethyl acrylate, vinyl acetate, a methyl ethyl ketone, etc., it is not limited to what was indicated.

[0013] the [Vth component] — as a hydrophobic monomer which suppresses the water solubility by the increment in II component, it adds as occasion demands and the amount used is 5 - 20% preferably 0 to 30%. Styrene, 1,3-butadiene, an isobutylene, 1-pentene, 2-pentene, a 2-methyl-1-butene, a 2-methyl-2-butene, a propylene, 1-octene, etc.

[0014] Generally in actual creation, the fizz microcapsule creation approach from the former is used. That is, a dispersant uses the gel of a colloidal silica system as a drainage system. A water soluble polymer compound is used as an auxiliary dispersant. As for a water soluble polymer compound, a diethanolamine-adipic-acid condensate, a polyvinyl pyrrolidone, methyl cellulose, etc. are used. Moreover, in order to use a lot of water-soluble monomers for this invention, an inorganic metal salt is used. The compound which dissolves in water as a water-soluble metal salt in neutrality, such as a sodium chloride, a magnesium chloride, sodium sulfate, a calcium chloride, and magnesium sulfate, or an acid field is used. More than 10% concentration of the water to be used is required for the amount used. If an inorganic metal salt is not used, even if it is hard to form a microcapsule and forms, by this monomer presentation, gas barrier nature will be inferior (the endocyst gas retention after 50 degree-C one-month preservation is 40% or

less). the above-mentioned mixture — pH 2-7 — it prepares to pH 2-5 preferably, and considers as a distributed drainage system.

[0015] An oil phase is mixed and used for homogeneity. Monomer mixture with partial saturation duplex association of radical reaction nature, the solvent mixture which has the boiling point below the softening temperature of an outside cereals polymer, and a radical initiator are used as an oil phase. By not dissolving in an outer wall polymer, although the organic solvent with which a solvent has the boiling point below **** temperature is used, although anything can be used if foaming effectiveness is high, the solvent of the hydrocarbon mold of the -20 - 100 boiling point range fits use. A petroleum fractional distillation component, such as n-butane, an isobutane, n pentane, an isopentane, a neopentane, n-hexane, an isohexane, n-heptane, and the other petroleum ether, is used timely.

[0016] The catalyst whose half-life temperature is 20 degrees or more is used for a radical initiator for 10 hours. as the catalyst which can be used — a peroxide mold and an azobis mold - - although any are sufficient, in order to carry out little content of the nitrile group in the initiator of an azobis mold at intramolecular — desirable — peroxidation — a snout — type or the azobis mold which does not contain a nitrile group is used. The thing of the 45-100 degree-C range has a preferably good 10-hour half-life 30 to 130 degree C. Although what does not specifically contain a nitrile group among diisopropyl peroxy carbonate, dioctyl peroxy dicarbonate, t-butyl-peroxy-laurate, lauroyl peroxide, dioctanoyl peroxide, benzoyl peroxide, azobisisobutyronitril, azobis (2,4-dimethylvaleronitrile), 1, and 1-azobis (cyclohexane-1-carbonitrile), dimethyl 2, 2'-azobis (2-methyl propionate), etc. is desirable, it is not limited to what was indicated.

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EXAMPLE

[Example] It is NaCl in 600g of example 1 ion exchange water. 200g is dissolved. 1g of adipic-acid diethanolamine condensates which are a ***** polymer is dissolved, and 100g of colloidal-silica 20% water solutions is added. This water solution is prepared to pH3.5, and it considers as the aqueous phase. Methacrylic acid methyl (MMA) 170g, methyl-acrylate (MA)10g, acrylic-acid (AA)20g, EDMA 1g, azobisisobutironitoriru 1g is mixed and it considers as a homogeneity solution. Let an isobutane in an autoclave be 50g preparation homogeneity solution at a monomer phase. After adding the aqueous phase here and adjusting particle diameter to ten to 25 micrometer, a nitrogen purge is carried out and it is made to react with the reaction temperature of 70 degrees C for 8 hours. Reaction pressure was performed by 0.8MPa(s) and stirring was performed by 500rpm. It was opened to traffic, although it cooled after reaction termination and let the screen of 150 meshes pass. It was air-dry after filtration. The particle size of the obtained microcapsule was 23 micrometers (a laser diffraction type particle-size-distribution measuring instrument (JEOL HELOS & RODOS (product made from German SYMPATEC GmbH)) is used for particle size, and it says the particle size used as 50% of accumulation of volume particle size distribution).

[0018] It coated on the test paper so that the obtained microcapsule might be mixed with an ethylene vinyl acetate system emulsion by the solid content ratio 2:1 and it might become 100-micrometer thickness at the time of desiccation. The heating foaming trial was performed in oven and it expanded to thickness 10 times in 130 degree-Cx 1 minute. The fizz of a microcapsule has 7 or more desirable times at 130 degree-Cx 1 minute, and is more desirable at 150 more degree-Cx 1 minute. [of 4 or more times] Moreover, although endocyst capacity was measured after one-month preservation at 50 degrees C in order to see the shelf life of the gas in a microcapsule, 80% of the initial intensive matter remained. In this invention, 60% or more, it is more desirable and manufacture of 80% or more of thing of the gas shelf life of a microcapsule is attained.

[0019] Example 2 aqueous phase is adjusted like an example 1. Methacrylic acid methyl (MMA) 55g, methacrylic acid ethyl (EMA) 55g, methyl-acrylate (MA)10g, acrylic-acid (AA)50g, (Styrene St) 30g, EDMA 1g and azobis (2,4-dimethylvaleronitrile) 1g are mixed, and it considers as a homogeneity solution. In an autoclave, 25g is taught to a monomer phase and let isobutane 25g and an isopentane be oil phases at it. After adding the aqueous phase here and preparing particle diameter to ten to 25 micrometer, a nitrogen purge is carried out and it is made to react with the reaction temperature of 60 degrees C for 8 hours. Reaction pressure was performed by 0.8MPa (s) and stirring was performed by 500rpm. The expansion scale factor was measured with the same test method as an example 1, and it expanded to thickness 12 times in 130 degree-Cx 1 minute. Moreover, although endocyst capacity was measured after one-month preservation at 50 degrees C in order to see the shelf life of the gas in a microcapsule, 95% of the initial intensive matter remained.

[0020] It manufactured like **** and the example 1 which show an example 3-12 in Table 1. [Table 1]

チストNo.	実施例1	実施例2	実施例3	実施例4	実施例5	実施例6	実施例7	実施例8	実施例9	実施例10	実施例11	実施例12
MMA	170	55	170	170	170	110	40		160	170	170	170
EMA		55						170				
VAc									20			
MA	10	10	10	10	10	10	20	10	20	10	10	10
AA	20		20	20	20	50	80	20	20		20	20
MAA										20		
St		80				30	60					
DVB											1	
EDMA	1	1	1	1	1	1	1	1	1	1		2
AIBN	1	1	1	1	1	1	1	1	1	1	1	1
イソブタン	50	25	30		30	50	50	50	50	50	50	50
イソペンタン		25	20									
イソヘキサン				50								
H ₂ O	600	600	600	600	600	600	800	600	800	600	600	600
NaCl	200	200	150	150			200	200	200	200	200	200
CaCl ₂						200						
MgCl ₂					200							
水溶性ポリアミド	2	2			2	2	2	2	2	2	2	2
メチルセルロース			2									
PVP				2								
反応温度 (°C)	70	60	70	70	70	70	70	70	70	70	70	70
反応時間 (hr)	8	8	8	8	8	8	8	8	8	8	8	8
粒径 (μm) (D ₅₀ %)	28	22	25	21	24	25	22	19	26	21	24	28
加熱温度 (°C)	130	130	140	150	130	130	130	120	130	140	130	130
加熱時間	1	1	1	1	1	1	1	1	1	1	1	1
発泡倍率	10.5	12.5	8.1	4.5	5	11.7	6.3	7.8	7.1	3.2	9.1	7.2
内包ガス量	17.5	20.0	18.1	19	11	17	18.4	17.8	18.2	18.5	18	17.7
内包ガス量 (50°C×1ヶ月)	14	18.9	16.2	18.5	8	16.0	16.1	14.1	15.0	14.3	13.9	14.1

[0021] The example of a comparison is given to Table 2.

When the examples 1 and 4 of a comparison and 5 acrylic acids are not used. Although foamed to the microcapsule which created the methyl methacrylate and the methyl acrylate as a principal component without the acrylic acid in the example 1 a little, there is no shelf life further low [expansion ratio], and outgassing happens immediately. Even if it changes a principal component similarly, when there is no acrylic acid, there are not fizz and a preservation ratio. It reacted by the example and the similar presentation except having made the amount of the example of comparison 2 acrylic acid used into 2.5%. In this case, the holdout of gas is bad although fizz is improved.

When the amount of the example of comparison 3 acrylic acid used was made into 50%, a microcapsule did not generate.

[0022]

[Table 2]

テストNo.	比較例1	比較例2	比較例3	比較例4	比較例5
MMA	180	185	90	150	150
St				30	
MA	20	10	10	20	
VAc					50
AA		5	100		
EDMA	1	1	1	1	1
AIBN	1	1	1	1	1
イソブタン	50	50	50	50	50
H ₂ O	600	600	600	600	600
NaCl	150	100	200	150	150
水溶性ポリアミド	2	2	2	2	2
コロイドシリカ	100	100	100	100	100
pH	3.5	3.5	3.5	3.5	3.5
反応温度 (°C)	70	70	70	70	70
反応時間 (hr)	8	8	8	8	8
粒径 (μm) (D _{x50} %)	23	21		27	25
加熱温度 (°C)	130	130		130	130
加熱時間 (分)	1	1		1	1
発泡倍率	3.1	3.5		2.7	2.1
内包量 (wt%)	17	18		17.5	17.3
内包量 (wt%) 50°C×1ヶ月	3.4	5.2		2.1	2.5

[Translation done.]